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Influence of Calcite and Dissolved Calcium on Uranium(VI) Sorption to a Hanford Subsurface Sediment

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The influence of calcite and dissolved calcium on U(VI) adsorption was investigated using a calcite-containing sandy silt/clay sediment from the U. S. Department of Energy Hanford site. U(VI) adsorption to sediment, treated sediment, and sediment size fractions was studied in solutions that both had and had not been preequilibrated with calcite, at initial [U(VI)] = 10^{-7}−10^{-5} mol/L and final pH = 6.0−10.0. Kinetic and reversibility studies (pH 8.4) showed rapid sorption (30 min), with reasonable reversibility in the 3-day reaction time. Sorption from solutions equilibrated with calcite showed maximum U(VI) adsorption at pH 8.4 ± 0.1. In contrast, calcium-free systems showed the greatest adsorption at pH 6.0−7.2. At pH > 8.4, U(VI) adsorption was identical from calcium-free and calcium-containing solutions. For calcite-presaturated systems, both speciation calculations and laser-induced fluorescence spectroscopic analyses indicated that aqueous U(VI) was increasingly dominated by $Ca_2UO_2(CO_3)_3^0$(aq) at pH < 8.4 and that formation of $Ca_2UO_2(CO_3)_3^0$(aq) is what suppresses U(VI) adsorption. Above pH 8.4, aqueous U(VI) speciation was dominated by $UO_2(CO_3)_3^{4-}$ in all solutions. Finally, results also showed that U(VI) adsorption was additive in regard to size fraction but not in regard to mineral mass: Carbonate minerals may have blocked U(VI) access to surfaces of higher sorption affinity.

Introduction

Uranium(VI) is a common contaminant at sites of nuclear materials processing and uranium mining (*1*, *2*). At the U. S. Department of Energy (DOE) Hanford site, groundwater containing U(VI) has a high probability of discharging to the nearby Columbia River (*3*). For this and other sites, an important aspect of both risk assessment and the evaluation of remediation alternatives is to project the rate of U(VI) migration in subsurface environments. In-ground mobility of uranium(VI) is typically controlled by sorption and desorption processes that are in turn influenced by U(VI) speciation and sorbent properties.

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U(VI) species can adsorb to phyllosilicates both by ion exchange to fixed charge sites (*4*, *5*) and by surface complexation with amphoteric hydroxyl edge sites (*4*−*6*). Surface complexation of U(VI) has been well-studied with hematite (*7*), goethite (*8*), ferrihydrite (*9*, *10*), quartz (*11*), clinoptilite (*12*), and gibbsite (*9*). Although ion exchange and surface complexation models have been developed for describing U(VI) adsorption to various minerals, such models are difficult to apply to natural sediments in a predictive sense, owing to difficulty in characterizing the quantity of available sites, especially for natural materials where some mineral phases occlude access to others.

Calcite is a known sorbent for various divalent cations including Mn^{2+}, Fe^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} (*13*−*15*), and U(VI) (*16*). Calcite is a minor mineralogical component in many sediments and typically exists as a form of cement or coating material that can aggregate other minerals and/or cover their surfaces (*17*, *18*). At the Hanford site, calcite is a common mineral component, with which porewater is often at equilibrium (*19*). Calcite can affect U(VI) adsorption to mineral assemblages through its direct role as an adsorbent but may also block sorbate access to other solids. Additionally, dissolved Ca^{2+} and carbonate from calcite can complex with U(VI) to form $Ca_2UO_2(CO_3)_3^0$(aq) and $UO_2(CO_3)_3^{4-}$ species at circumneutral to alkaline pH conditions (*20*, *21*). In fact, $Ca_2UO_2(CO_3)_3^0$(aq) has been found to be a major aqueous U(VI) species in the vadose porewater at the Hanford site (*19*, *22*). A recent study (*23*) showed that the presence of calcium carbonate in soils can suppress U(VI) sorption in the pH range of about 6−9 and that calcite can be a source of dissolved calcium for the formation of the neutral U(VI) complex ($Ca_2UO_2(CO_3)_3^0$(aq)) (*23*).

In this study, we investigated the influence of calcite ($CaCO_3$(s)) and aqueous calcium on U(VI) adsorption with a calcite-containing sediment from the U. S. DOE Hanford site. U(VI) adsorption was studied onto collected Hanford sediment, its size fractions, and both untreated (carbonate-containing) and treated (carbonate-free) samples of the silt/clay fraction. These studies were conducted at circumneutral pH to alkaline/calcareous conditions that are representative of the Hanford groundwater system. The aqueous U(VI) speciation was monitored using laser-induced fluorescence spectroscopy (LIFS) and also calculated using equilibrium speciation models. The results were also used to test whether U(VI) adsorption to the whole sediment material could be conceived as an additive process in terms of either size fractions or mineral components.

Materials and Methods

Materials. The sediment used in this study was a composite of sand- and silt-sized aggregates of finer grained materials that were collected from a background borehole (RCRA borehole #299-W22-48, ref *24*) beneath the U. S. DOE Hanford site at selected depth intervals between 42 and 44 m below the ground surface. Nearby U(VI) plumes exist in these same sediment types. The pH in porewater and groundwater at the Hanford site is variable, mostly ranging from 6.5 to 10 depending on specific locations (*24*). Sediment in the zone of sampling was largely dominated by quartz (∼45−95%), plagioclase feldspar (∼10−20%), and alkali feldspar (∼20−40%) (*24*). Specific XRD analysis of the Hanford silt composite (HSC) sample (unpublished data, Pacific Northwest Laboratory, 2004) revealed that the major mineral components of the composite are quartz (SiO_2), albite ($NaAlSi_3O_8$), clinochlore [$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$], potassicpargasite [$KCa_2(Mg_3FeAl)(Si_6Al_2)O_{22}(OH)_2$], and muscovite [$KAl_2(Si_3Al)$-

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$O_{10}(OH,F)_2$]. Calcite ($CaCO_3$(s)) was also detected by the XRD as a minor component, and inorganic carbon has been quantified (see below).

The air-dried composite sediment (referred to as the Hanford silt composite, HSC) was split into two portions with a two-way splitter. One portion was stored as the originally composited sample (hereafter referred to as the original HSC), and the other was separated into a sand fraction and a finer sized fraction (hereafter referred to as the HSC silt/clay fraction) by suspending the original HSC in deionized water and wet-sieving through a 53-μm mesh. The size fractions were air-dried or further treated to remove specific mineralogical components before further splitting for use in U(VI) adsorption experiments.

Pure calcite powder was used as a model compound to study U(VI) adsorption to carbonate minerals. Calcite crystals (rhombic cleavage, Sargent-Welch Scientific, Buffalo Grove, IL) were pulverized to a fine powder (<200 μm) with a Shatterbox (model 8511, Spex Industries Inc., NJ).

Sediment Treatments. For the removal of carbonate minerals, one portion of the HSC silt/clay fraction was treated with a 1 mol/L sodium acetate solution at pH 5.0 (adjusted with acetic acid). The treatment followed a procedure described by Zachara et al. (*25*), but with a minor modification as described in the Supporting Information (SI). The remaining materials after treatment (hereafter referred to as the carbonate-free HSC silt/clay) were air-dried, homogenized, and split into two fractions, one of which was used directly for U(VI) adsorption experiments and the other of which was further treated to remove iron (hydr)oxides.

Iron (hydr)oxide-extracted sediment was prepared by chemical treatment of the carbonate-free silt/clay with a dithionite−citrate−bicarbonate (DCB) solution (*26*). Details of the DCB extraction can be found in the SI.

Electrolytes. Calcite-saturated and Ca^{2+}-free electrolyte solutions were used in the study of U(VI) adsorption. Ca^{2+}-free solutions with a pH ranging from 6 to 10 and an ionic strength (I) of 0.05 mol/L were prepared by appropriate additions of Na_2CO_3−$NaHCO_3$, $NaNO_3$, HNO_3, or NaOH and were maintained in equilibrium with atmospheric CO_2(g) by bubbling with air. Calcite-saturated electrolyte solutions in the pH range from ~7.2 to 10 were also made at $I = 0.05$ mol/L by mixing appropriate Ca^{2+}-free electrolyte solutions with excess calcite powder ($CaCO_3$(s)) and allowing the resulting suspensions to equilibrate for 3 days with atmospheric CO_2(g) (*27*). The calcite-equilibrated solutions had a stable pH and were filtered through a 0.2-μm membrane filter to remove solid-phase calcite before use in adsorption experiments.

U(VI) Adsorption. U(VI) batch adsorption experiments were conducted in 5-mL or 10-mL polyethylene centrifuge tubes at a solid/liquid ratio of 100 g/L. Preliminary experiments with various solid/liquid ratios (10−500 g/L) at pH 8.4 indicated that U(VI) adsorption increased with increasing solid/liquid ratio in a manner that was consistent with the soil−water distribution coefficient (K_d) and independent of the solid/liquid ratio. A ratio of 100 g/L was selected based on a criterion of achieving a supernatant U(VI) concentration that was sufficient for measurement while still maintaining measurable amounts of uptake. Final uptake from solution was in the range of 20−80% for most experiments. Preliminary kinetic experiments conducted at pH 8.4 up to 72 h indicated that the extent of U(VI) adsorption reached a stable plateau (taken to represent equilibrium) within 30 min. Details of the kinetic results may be found in the SI (Figure S-1). All subsequent sorption experiments were conducted with 72 h of equilibration for consistency with preliminary studies that had been conducted for that duration.

For all experiments, the solid samples were equilibrated with either calcite-saturated or Ca^{2+}-free electrolyte solutions prior to addition of U(VI). The solid suspensions were continuously mixed by end-over-end rotation of sorption vessels at 45 rpm for 3 days (model 099A RD4512, Glas-Col Rotator Co., Terre Haute, IN) and centrifuged at 2100*g* for 30 min, after which the supernatants were decanted and replaced with fresh calcite-saturated or Ca^{2+}-free solution and the process was repeated. After three such equilibration cycles, stable pH values were observed in all of the test suspensions. For the fourth replacement, the amount of remaining supernatant was gravimetrically determined, and the samples then were spiked with an appropriate volume of clean electrolyte solution and a small volume (~50−100 μL) of concentrated $UO_2(NO_3)_2$ stock solution as needed to achieve the desired initial [U(VI)]. A small volume of NaOH solution was added to neutralize the acidity introduced by the U(VI) stock solution, which was kept at pH ≈ 1.5 to avoid precipitation of solids (such as schoepite). The estimated volume error from addition of U(VI) stock and NaOH solutions was less than 1%. The U(VI)-spiked tubes were equilibrated for 3 days on the rotator shaker and kept in equilibrium with atmospheric CO_2 by opening the tube caps frequently and replacing the headspace (~3−5 mL) with fresh air. After equilibration, the suspensions were centrifuged at 2100*g* for 30 min, and the supernatants were measured for pH and aqueous U(VI) concentration. The adsorbed U(VI) was calculated as the difference between total added U(VI) and equilibrium aqueous U(VI). All experiments were conducted with duplicate samples. At the end of each adsorption experiment, U(VI) desorption was investigated by adding fresh U(VI)-free, calcite-saturated solution. After 3 days allotted to the desorption, U(VI) in the supernatant was measured. These results suggest that the U(VI) adsorption onto untreated silt/clay fraction is reasonably reversible. (See Figure S-2 and associated discussion in the SI.)

Control experiments at pH 8.4 were used to quantify the background U(VI) concentration in electrolytes and soils and U(VI) losses to tube walls. Both effects were negligible; see the SI.

Measurements. Total and organic carbon contents in the sediment were measured by a coulometric analysis of CO_2 following high-temperature combustion (combustion furnace, CM5030; CO_2 coulometer, model 5012, UIC Coulometrics Inc., IL). Prior to the measurement of total organic carbon, the sediment samples were treated with 1 mol/L HCl to remove inorganic carbonate minerals and dried at 80 °C. The difference between the total and organic carbon contents was reported as inorganic carbon. The iron (hydr)oxide content was determined using a citrate−dithionite extraction (*28*).

Aqueous U(VI) concentration was measured with a kinetic phosphorescence analyzer (KPA) (KPA-11, Chemcheck Instruments Inc., Richland, WA). For the KPA analysis, U(VI) samples were acidified to about pH = 1 prior to analysis using 0.2−1.0 mol/L HNO_3 solutions. Some samples were diluted with enough 0.1 mol/L HNO_3 to decrease the Ca concentration below 10^{-3} mol/L as necessary to minimize its interference in the U(VI) measurement (*29*). With these treatments, the effective KPA detection limit was 0.1 μg/L. pH was measured using a combination electrode (model 13-620-530, Fisher Scientific, NJ).

LIFS Analysis. Laser-induced fluorescence spectra (LIFS) of aqueous samples in calcite-saturated or Ca^{2+}-free solutions were recorded from 450 to 600 nm at near liquid helium temperature (LHeT = 6 ± 1 K) to determine aqueous U(VI) speciation. Details of the LIFS analysis are described in the SI.

Results and Discussion

Solids Characterization. The HSC sediment was found to consist of roughly 31% sand (>53 μm), 61% silt (2−53 μm),

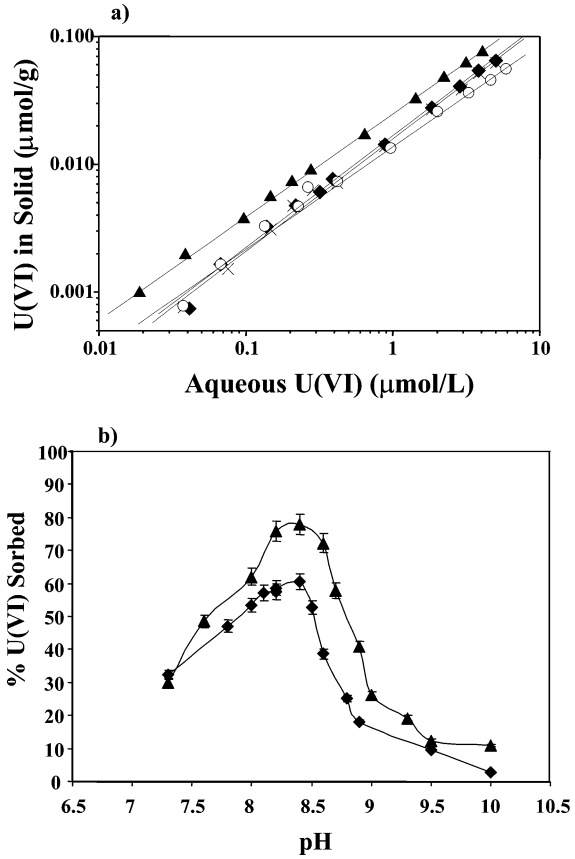

FIGURE 1. (a) U(VI) sorption isotherms for four materials in calcite-presaturated solutions at pH = 8.4 ± 0.1 and $P_{CO_2} = 10^{-3.5}$ atm: ▲ = carbonate-free HSC silt/clay; ♦ = untreated HSC silt/clay; × = pure calcite; ○ = original HSC. (Initial [U(VI)] ranged from 1.0 × 10^{-7} to 1.0 × 10^{-5} mol/L, solid/solution ratio = 100 g/L, I = 0.05 mol/L ($NaNO_3$), and T = 22.5 °C.) (b) U(VI) sorption as a function of pH in calcite-presaturated solutions at $P_{CO_2} = 10^{-3.5}$ atm: ♦ = untreated HSC silt/clay; ▲ = carbonate-free silt/clay. (Initial [U(VI)] = 1.2 × 10^{-6} mol/L, solid/solution ratio = 100 g/L, I = 0.05 mol/L ($NaNO_3$), and T = 22.5 °C).

and 6% clay (<2 μm) by weight. Total and organic carbon contents in the original HSC were found to be 3.6 and 0.57 mg/g, respectively, implying 3.0 mg/g of inorganic carbon, or 0.025 g/g as $CaCO_3$(s). Total and organic carbon contents in the untreated HSC silt/clay fraction (<53 μm) were 4.1 and 0.51 mg/g, respectively, implying an inorganic carbon content of 3.6 mg/g, or 0.030 g/g as $CaCO_3$(s). For the sand fraction, the total and organic carbon contents were 2.3 and 0.74 mg/g, respectively, implying 1.6 mg/g of inorganic carbon, or 0.013 g/g as $CaCO_3$(s). The inorganic carbon content remaining in the treated silt/clay fraction was below the detection limit. Iron (hydr)oxides were found to be less than 1% by mass in the carbonate-free silt/clay size fraction.

U(VI) Adsorption and the Role of Carbonate Minerals. U(VI) adsorption isotherms are shown in Figure 1a for four materials under conditions of identical water chemistry that include calcite-saturated suspensions at ambient P_{CO_2}, constant ionic strength (0.05 mol/L), and pH = 8.4 (±0.1). Isotherms for all four materials (original HSC, HSC silt/clay, carbonate-free HSC silt/clay, and pure calcite) are nonlinear overall, with fitted Freundlich exponents between 0.80 and 0.88. (See Table S-2 in the SI for details.) Interestingly, all samples except the carbonate-free HSC silt/clay (solid triangles) show substantially greater isotherm linearity at [U(VI)] < ~0.3 μmol/L. (A linear relation, i.e., $S = K_f C$, is shown by isotherm slopes approaching 1.0 on the log−log plot of Figure 1a.) U(VI) adsorption to the pure calcite was approximately the same as that for the HSC silt/clay fraction (K_d value at C_e of 1 μmol/L = 16 mL/g for both materials; Table S-2), and adsorption to both of these was slightly higher than that to the original HSC (K_d value at C_e of 1 μmol/L = 14 mL/g; Table S-2). These results implied that calcite could serve as a mineral component for U(VI) adsorption in this sediment. Removal of the minor (only ~3%) mass fraction of carbonate minerals was found, however, to cause an approximately 50% increase in U(VI) adsorption in the HSC silt/clay fraction relative to untreated samples of this same material (K_d value at C_e of 1 μmol/L = 24 mL/g for treated vs 16 mL/g for untreated; Table S-2). The extent of increase cannot be explained by mass additivity relations, even if sorption to the removed minerals was negligible. The degree of nonadditivity is of course even more extensive if the removed carbonates are assumed to sorb U(VI) in a similar matter as pure calcite. In either case, these results indicate that U(VI) adsorption to underlying minerals in the HSC silt/clay fraction was stronger than adsorption to exposed mineral surfaces in untreated samples of the same material. We speculate that the carbonate minerals existed as cementing and/or surface-coating phases (*17*, *18*) that block U(VI) access to higher-affinity sites on these silts and clays.

Figure 1b shows U(VI) adsorption from calcite-presaturated solutions of fixed initial U(VI) concentration (1.2 μmol/L) to both the untreated and the acetic-acid-treated (carbonate-free) silt/clay fractions. As evident from this figure, U(VI) adsorption to both fractions was maximum at pH 8.4. As explained in the next section, the declining sorption at circumneutral pH reflects the effects of calcium on U(VI) speciation. For purposes of current discussion (comparisons among solids from solutions of essentially identical aqueous chemistry), we note that removal of carbonate minerals from the HSC silt/clay led to increased U(VI) adsorption at all pH values above 7.2 and that the largest increase (~20%) was observed in the pH range from 8.2 to 8.8. Thus, the surfaces that were exposed by treatment apparently have a higher affinity for U(VI) than the removed carbonate mineral surfaces over a wide range of pH values.

Influence of Aqueous Ca^{2+}. Figure 2a compares U(VI) adsorption onto acid-treated (carbonate-free) HSC silt/clay as a function of pH, using electrolyte solutions of equivalent P_{CO_2} and ionic strength but with (solid triangles) or without (open triangles) solution presaturated with calcite. Below pH 8.4, U(VI) adsorption was substantially lower for the systems using calcite-presaturated solutions than that in the Ca^{2+}-free systems (Figure 2a). Whereas adsorption from the calcite-saturated electrolyte solution shows steadily decreasing sorption as pH drops below 8.4 (Figure 2a), the fraction of U(VI) adsorbed from Ca^{2+}-free electrolyte is nearly 100% for all pH values below 7.2 and is >80% up through pH 8.4. This behavior is similar to that typically reported in the literature for U(VI) adsorption to clean minerals as a function of pH and in the presence of aqueous carbonate but not calcium (e.g., refs *30* and *31*). Above pH 8.4, the U(VI) adsorption in the two systems was almost identical. Also, comparison among the two open-symbol plots in Figure 2a (upright and upside-down triangles) shows that removal of iron (hydr)oxides had no effect on the U(VI) adsorption. Given that iron (hydr)oxides are in low concentration in this material (<1%), it is unlikely that these minerals play an important role in this system. It is more likely that the higher-affinity sites were associated with the edges of phyllosilicate minerals in the sediments, which can strongly complex with aqueous U(VI) (*4*−*6*).

Figure 2b shows that results with the untreated (carbonate-containing) silt/clay fraction in initially calcite-saturated solutions (solid diamonds) are similar to those in initially Ca^{2+}-free solutions (open diamonds). These results suggest that dissolved calcium from the untreated silt/clay fraction

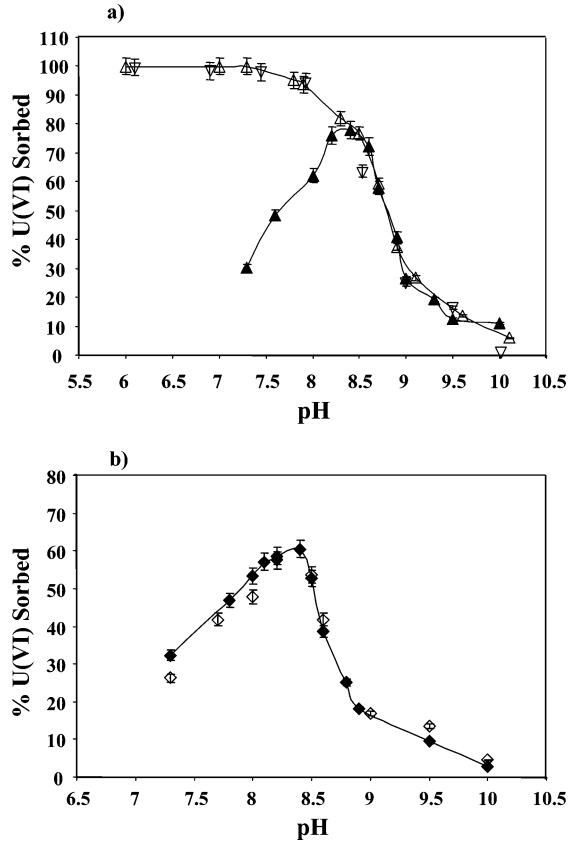

FIGURE 2. U(VI) sorption as a function of pH in five systems. (a) Three sorption systems with acid-washed solids: ▲ = carbonate-free HSC silt/clay in calcite-presaturated solution; △ = carbonate-free HSC silt/clay in Ca^{2+}-free solution; ▽ = both carbonate- and iron-(hydr)oxide-free silt/clay in Ca^{2+}-free solution. (Initial [U(VI)] = 1.2×10^{-6} mol/L, solid/solution ratio = 100 g/L, I = 0.05 mol/L ($NaNO_3$), $P_{CO_2} = 10^{-3.5}$ atm, and T = 22.5 °C). Note that only the systems with open symbols are calcium-free. (b) Two sorption systems with untreated HSC silt/clay: ♦ = untreated HSC silt/clay with calcite-presaturated solution; ◊ = untreated HSC silt/clay with initially Ca^{2+}-free solution. (Initial [U(VI)] = 1.2×10^{-6} mol/L, solid/solution ratio = 100 g/L, I = 0.05 mol/L ($NaNO_3$), $P_{CO_2} = 10^{-3.5}$ atm, and T = 22.5 °C.) Note that neither system is calcium-free at equilibrium conditions.

can affect sorption in a similar manner as that brought into solution through calcite presaturation. In fact, the amount of carbonate minerals in this untreated HSC silt/clay were calculated to be more than sufficient to provide solution saturation with respect to calcite during U(VI) adsorption equilibration, even for cases where the added water was initially free of calcium. A comparison of the dissolved calcium concentrations in these systems as obtained from calculations (based on known pH, P_{CO_2}, and calcite solubility) and measurement (by inductively coupled plasma (ICP)−OES) is presented in the SI.

Overall, the results show that those systems without Ca^{2+} in solution had much stronger U(VI) sorption in the pH range from 7.2 to 8.4. The results are best understood in conjunction with our results for the calculated and observed U(VI) speciation, as described below.

U(VI) Speciation Calculations and Implications for Sorption. Aqueous U(VI) speciation in both calcite-saturated (Figure 3) and Ca^{2+}-free suspensions (Figure S-3 of the SI) were calculated using FITEQL 4.0 (*32*) with a database assembled by the authors from the literature (*21*, *33*). In the calcite-saturated sorption suspensions, a ternary species [$Ca_2UO_2(CO_3)_3^0$(aq)] was calculated to be the dominant species at pH values below 8.4 (Figure 3). This is in contrast to the

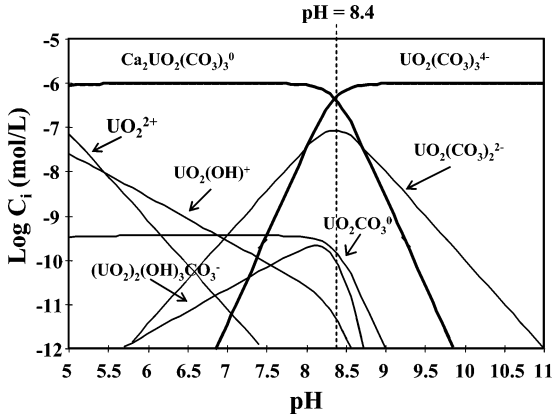

FIGURE 3. U(VI) speciation in calcite-presaturated solution at $P_{CO_2} = 10^{-3.5}$ atm. ([U(VI)] = 1.0×10^{-6} mol/L, I = 0.05 mol/L ($NaNO_3$), and T = 25 °C.) The complexation constants of all species are from Grenthe et al. and Kalmykov and Choppin (*21*, *33*).

situation in Ca^{2+}-free suspensions (Ca^{2+}-free electrolyte with carbonate-free silt/clay) where $(UO_2)_2(OH)_3CO_3^-$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ were calculated to be the dominant species at pH 6.4−10. (See Figure S-3 in the SI and Figure 2a in ref *30*.) Above pH 8.4, $UO_2(CO_3)_3^{4-}$ was calculated to be dominant in both calcite-saturated and calcium-free systems.

Given that the aqueous $Ca_2UO_2(CO_3)_3^0$ complex is expected in the calcite-saturated supernatants either for untreated HSC silt/clay or for carbonate-free silt/clay, the differences in U(VI) adsorption from pH 7.2 to 8.4 (Figures 2a and 2b) are most likely due to the dominant presence of $Ca_2UO_2(CO_3)_3^0$(aq) (or closely related species) at pH < 8.4 in the calcium-containing systems. By contrast, the similarity of results at pH > 8.4 for all systems (Figures 1b, 2a, and 2b) is in agreement with calculations that suggest the dominance of a single species ($UO_2(CO_3)_3^{4-}$) at high pH in all of the systems. Some of these predicted speciation differences can also be directly measured through LIFS, as described below.

U(VI) Speciation Measurements (LIFS). For samples with higher concentrations of dissolved calcium, the LIFS analysis of the sorption suspension supernatants showed moderate to intense U(VI) fluorescence spectra at LHeT with well-resolved vibronic bands with spectral origins at ~480 nm (Figure 4 and Table 1). By contrast, the samples containing calcium-free suspensions (carbonate-free HSC silt/clay and Ca^{2+}-free electrolyte) showed weak and noisy LIFS spectra because U(VI) was primarily partitioned to the solid phase (Figure 2a). The well-resolved LIFS spectra (Figure 4) possess the basic structure of uranyl-tricarbonate in which the three carbonate groups are coordinated along the equatorial plane of the uranyl ion as bidentate ligands (*34*−*37*). A careful examination of the LIFS spectra revealed that for the suspension supernatants with calcite-saturated electrolytes at circumneutral pHs (shown as traces 4 and 8 at pH 7.3 in Figure 4 and Table 1) the spectral positions were shifted ~ 2 nm to longer wavelengths as compared to those at higher pH values (shown as traces 5 and 7 at pH 8.3 and 8.5 in Figure 4 and Table 1). Comparisons of these spectral features with those of aqueous species $Ca_2UO_2(CO_3)_3^0$(aq) and $UO_2(CO_3)_3^{4-}$ (traces 2 and 3, respectively, in Figure 4) suggest that $Ca_2UO_2(CO_3)_3^0$(aq) dominated aqueous uranyl speciation in the calcite-saturated suspensions at circumneutral pHs, while $UO_2(CO_3)_3^{4-}$ dominated above pH 8.3. The removal of carbonate minerals from the sediment did not alter the supernatant U(VI) speciation if the electrolyte was equilibrated with calcite—compare trace 8 (carbonate-free) to trace 4 (untreated).

The measured U(VI) speciation was generally consistent with the calculated speciation, although noticeable differ-

TABLE 1. LHeT Fluorescence Spectral Characteristics of Aqueous U(VI) Species after U(VI) Adsorption Equilibration ($P_{CO_2} = 10^{-3.5}$ atm and $\lambda_{ex} = 415$ mm)

sample ID[a]	sample	spectral maxima (nm)	major species
1	UO_2^{2+} [b,c]	491.7, 513.9, 538.4, 563.5	UO_2^{2+}
2	$Ca_2UO_2(CO_3)_3^0$(aq)[b]	480.5, 501.2, 522.7, 546.0	$Ca_2UO_2(CO_3)_3^0$(aq)
3	$UO_2(CO_3)_3^{4-}$ [b]	479.6, 499.2, 519.9, 542.4	$UO_2(CO_3)_3^{4-}$
4	supernatant: untreated HSC silt/clay; calcite-presaturated solution, pH = 7.3	481.2, 502.0, 521.9, 545.5	$Ca_2UO_2(CO_3)_3^0$(aq))
5	supernatant: untreated HSC silt/clay; calcite-presaturated solution, pH = 8.3	478.7, 499.0, 519.7, 543.3	$UO_2(CO_3)_3^{4-}$
6	supernatant: untreated HSC silt/clay; initially Ca^{2+}-free solution, pH = 7.3	478.7, 499.0, 520.2, 543.0	$UO_2(CO_3)_3^{4-}$
7	supernatant: untreated HSC silt/clay; initially Ca^{2+}-free solution, pH = 8.5	478.4, 499.0, 520.8, 543.0	$UO_2(CO_3)_3^{4-}$
8	supernatant: carbonate-free HSC silt/clay; calcite-presaturated solution, pH = 7.3	480.6, 500.6, 522.2, 544.9	$Ca_2UO_2(CO_3)_3^0$(aq)
9	supernatant: carbonate-free HSC silt/clay; initially Ca^{2+}-free solution, pH = 7.3	478.4, 500.1, 521.3, 544.7	$UO_2(CO_3)_3^{4-}$

[a] Trace number in Figure 4. [b] Data from ref 37. [c] Uranyl exists as the UO_2^{2+} ion and/or its complexes with nitrate.

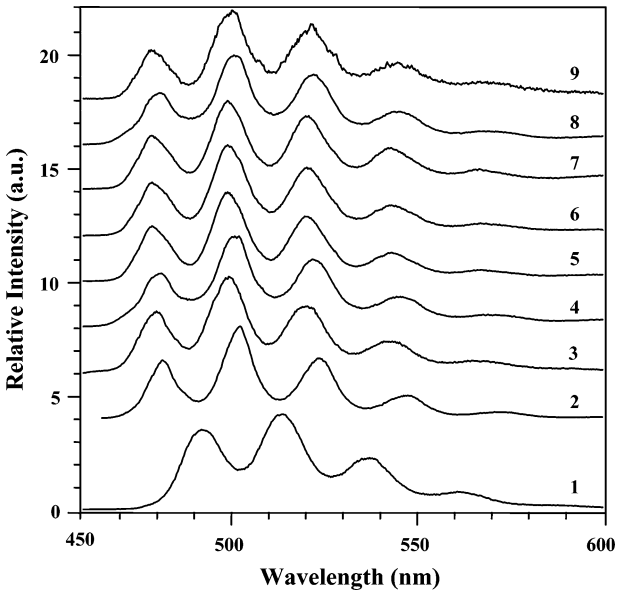

FIGURE 4. LHeT fluorescence spectra at $\lambda_{ex} = 415$ nm for (1) a standard solution of aqueous UO_2^{2+}(aq), (2) a standard solution of $Ca_2UO_2(CO_3)_3^0$(aq), (3) a standard solution of $(UO_2)(CO_3)_3^{4-}$(aq), and samples of the following six sorption vessel supernatants (centrates): (4) after contact with untreated HSC silt/clay using calcite-presaturated solution, [U(VI)] = 7.5×10^{-7} mol/L, pH = 7.3; (5) after contact with untreated HSC silt/clay using calcite-presaturated solution, [U(VI)] = 4.6×10^{-7} mol/L, pH = 8.3; (6) after contact with untreated HSC silt/clay using initially Ca^{2+}-free solution, [U(VI)] = 9.2×10^{-7} mol/L, pH = 7.3; (7) after contact with untreated HSC silt/clay using initially Ca^{2+}-free solution, [U(VI)] = 5.2×10^{-7} mol/L, pH = 8.5; (8) after contact with carbonate-free HSC silt/clay using calcite-presaturated solution, [U(VI)] = 7.8×10^{-7} mol/L, pH = 7.3; (9) after contact with carbonate-free HSC silt/clay using initially Ca^{2+}-free solution, [U(VI)] = 2.5×10^{-7} mol/L, pH = 7.3. The detailed solution compositions are given in Table 1 and $P_{CO2} = 10^{-3.5}$ atm for all samples. For clarity, the spectra were normalized to the same maximum intensities and offset along the vertical axis.

ences were present. In particular, species $Ca_2UO_2(CO_3)_3^0$(aq) was calculated to dominate up to pH 8.4 (Figure 3), while the LIFS spectra indicated that species $UO_2(CO_3)_3^{4-}$ dominated at pH 8.3 (Figure 4 and Table 1). There was likely a more gradual transition of U(VI) aqueous species dominance from $Ca_2UO_2(CO_3)_3^0$(aq) to $UO_2(CO_3)_3^{4-}$ as the pH increased from 7.0 to 10.0, relative to the calculated result that shows a sharp transition at pH 8.4 (Figure 3). A stability constant of log $K = 29.8$ (*21*) for $Ca_2UO_2(CO_3)_3^0$(aq) was used in this calculation. A lower stability constant of log $K = 26.8$ ($I = 0.1$ mol/L) has also been reported for this species (*38*). If an averaged value of log $K = 28.3$ from these two sources is used, then the calculated stability field of $Ca_2UO_2(CO_3)_3^0$(aq) shifts to a lower pH range and is more consistent with the LIFS measurements.

In the untreated sediment suspensions with initially Ca^{2+}-free electrolyte solution, the LIFS spectral peaks shifted only slightly toward longer wavelengths in the pH 7.3 sample (Figure 4, trace 6), compared with those in the sample at pH 8.3 (Figure 4, trace 7). The LIFS peaks were also slightly broadened toward longer wavelengths in the pH 7.3 sample. The difference was, however, small, and in both samples, the LIFS spectra were close to those of $UO_2(CO_3)_3^{4-}$ (Figure 4 and Table 1). These LIFS results are somewhat in contrast with expectations, based on sorption results and speciation calculations. The slight LIFS peak shift and broadening toward longer wavelengths in the pH 7.3 sample may indicate the presence of other unknown species in the system that affect U(VI) adsorption in a similar way as $Ca_2UO_2(CO_3)_3^0$(aq). The measurement of stability constants for species $Ca_2UO_2(CO_3)_3^0$(aq) has suggested that a species $CaUO_2(CO_3)_3^{2-}$ can become increasingly dominant at a decreasing ratio of Ca^{2+} to U(VI) (*21*). Unfortunately, further evaluation of these results is limited by a still incomplete understanding of the thermodynamics and LIFS spectra for $CaUO_2(CO_3)_3^{2-}$ and other potential species in the calcium−uranyl−carbonate system.

Size Fraction Additivity. U(VI) was adsorbed to both silt/clay and sand size fractions under the studied pH range (Figure 5). Below pH 9, U(VI) adsorbed more strongly to silt/clay than to the sand fraction, on a unit mass basis. Above pH 9, however, the U(VI) adsorption was stronger to the sand fraction. A U(VI) adsorption peak near pH 8.4 was again observed in the original HSC sediment and its size fractions. U(VI) adsorption to the original HSC was approximately between those to the silt/clay and sand fractions and was close to the amount calculated by a linear additivity approach (solid line). The calculation was made by a linear, mass-weighted combination of adsorbed U(VI) in the sand and silt/clay fractions—that is, $K_{d(HSC)} = f_{silt/clay} K_{d(silt/clay)} + f_{sand} K_{d(sand)}$, where $f_{silt/clay}$ and f_{sand} are the mass fractions (wt %) of the silt/clay and sand in the original HSC, respectively; $K_{d(silt/clay)}$ and $K_{d(sand)}$ are the adsorbed U(VI) distribution coefficients (mL/g) in the suspensions of silt/clay and sand fractions, respectively; $K_{d(HSC)}$ is the overall distribution coefficient (mL/g) in the original HSC system. The relationship between adsorption percentage (%$U(VI)_{sb}$) and distri-

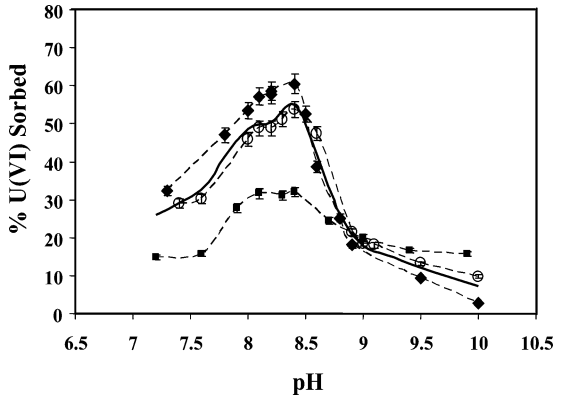

FIGURE 5. U(VI) sorption as a function of pH for the original HSC and two size fractions at $P_{CO_2} = 10^{-3.5}$ atm: ○ = original HSC; ♦ = untreated HSC silt/clay; ■ = untreated HSC sand. The solid line is the estimate of original HSC sorption as calculated from the CA approach. (Initial [U(VI)] = 1.2×10^{-6} mol/L, solid/solution ratio = 100 g/L, I = 0.05 mol/L ($NaNO_3$), and T = 22.5 °C.)

bution coefficient (K_d, mL/g) is given by the equation: $\%U(VI)_{sb} = K_d/(K_d + V/m)$, where V/m is the ratio of solution volume to solid mass, which is a constant in this study (10 mL/g).

Component Additivity. With the component additivity (CA) approach (*39*−*42*), U(VI) adsorption to the mineral assemblage or sediment would be the simple mass-weighted sum of mass-based U(VI) adsorption estimates for the individual mineral components. Our results clearly indicate, however, that such a CA approach is not applicable to the consideration of carbonate minerals in the HSC silt/clay materials. Although carbonate minerals are minor (∼3%) components of the silt/clay material and calcite can individually adsorb U(VI), our results show that carbonate removal from this material caused substantial increases in U(VI) adsorption (∼50%) (Figure 1). Thus, a more complex and mechanistically rigorous CA approach would be required, perhaps as based on a more complete understanding of the variety of *exposed surfaces* and their relative contributions to sorption. In the absence of such understanding, however, it is necessary to directly characterize U(VI) adsorption to the actual mineral assemblages as they exist in situ.

Expected Effects on U(VI) Transport. Overall, our results imply that the presence of calcite (at concentrations present in the original HSC solids) may act to increase U(VI) mobility in the Hanford subsurface because the calcite can (1) prevent access to U(VI) adsorption onto higher-energy adsorption sites in the silt/clay fraction and (2) provide a source of calcium and carbonate to water that promotes the formation of a ternary uranyl aqueous species $Ca_2UO_2(CO_3)_3^0(aq)$, which effectively competes with surface sites for the complexation of U(VI). Note that both effects will cause increased U(VI) mobility at circumneutral to mildly alkaline subsurface environments. Thus, the assessment of U reactive transport at this site or others with similar geochemical conditions will need to consider the influence of calcite and carbonate minerals as U(VI) sorbents, as inhibitors of U(VI) access to potentially higher-affinity U(VI) adsorption sites of other minerals, and as contributors of dissolved divalent cations and carbonate that can affect U(VI) aqueous speciation and adsorption.

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Supporting Information Available

Removal of carbonate minerals from sorbent solids, removal of free iron (hydr)oxides from sorbent solids by the DCB method, U(VI) sorption kinetics study, U(VI) desorption study, study of background U(VI) concentrations in sediments and of U(VI) loss to reaction vessels during U(VI) adsorption experiments, analysis of Ca^{2+} concentrations in sorption supernatants, investigation of soil−solution separation methods on U(VI) equilibrium concentration measurements, LIFS analysis, calculation of U(VI) speciation in calcium-free solution, and Freundlich parameters of U(VI) sorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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